THE MECHANISM OF REDUCTION OF ACID SODIUM TUNGSTATES AND THE FORMATION OF BRONZES

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Researches of a series of authors [1,2,3,4] have established that whereas the electrolysis of fused neutral sodium tungstate leads to separation of metallic tungsten at the cathode, electrolysis of acid tungstates gives tungsten bronzes.

In the present research a study was made of the mechanism of reduction of acid tungstates by metallic sodium and of the conditions of formation of tungsten bronzes.

The mechanism of reduction of acid tungstates by hydrogen was studied by V. I. Spitsyn [5]. He showed that during the first stage of the process the acid tungstate loses an atom of oxygen to form the corresponding bronze. Later the reduction proceeds in the temperature interval of 550-700° in strictly consecutive order from a less reduced to a more reduced bronze with separation of the metal: blue bronze $-Na_2W_5O_{15}[Na_2O\cdot(WO_3)_4WO_2]$; violet bronze $-Na_2W_4O_{12}[Na_2O(WO_3)_3\cdot WO_2]$; red bronze $-Na_2W_3O_9[Na_2O(WO_3)_2\cdot WO_2]$; golden-yellow bronze $-Na_2W_2O_6[Na_2O\cdot WO_3\cdot WO_2]$.

The final product of reduction is neutral tungstate and metal.

Brunner [6] prepared bronzes by fusion of neutral or acid tungstate with tungsten dioxide in absence of air according to the equation:

$$Na_2WO_4 + WO_2 = Na_2W_2O_6;\quad Na_2WO_4 + WO_3 + WO_2 = Na_2W_3O_9 \text{ etc.}$$

Philipp [7] obtained bronzes by reduction of acid tungstates with tin. He also showed that by fusion of bronzes with strongly acid or neutral tungstates it is possible to obtain bronzes respectively enriched or impoverished in tungsten trioxide. This method permits transition from one bronze to another.

Spitsyn and Cherepnev [8], when investigating the electrical conductivity of fused acid sodium tungstates, came to the conclusion that these compounds dissociate in melts with formation of free tungsten trioxide. A similar conclusion may be reached on inspecting the shape of the curve of the fusion diagram of the system sodium tungstate-tungsten trioxide.

It was previously shown that the first stage of the reaction of acid tungstates with sodium is marked by reduction of the free tungsten trioxide which is always present in the melt due to dissociation of the acid tungstate. Reduction of the trioxide proceeds according to the equations:

$$WO_3 + 6Na = 3Na_2O + W, \quad (1)$$

$$3Na_2O + 3WO_3 = 3Na_2WO_4, \quad (2)$$

or overall:

$$4WO_3 + 6Na = 3Na_2WO_4 + W. \quad (3)$$

Reaction (1) is a reaction of the eighth order and it is most unlikely that it takes place in one step. A more reasonable assumption is that reaction (1) proceeds through certain intermediate stages the first of which consists in reduction of tungsten trioxide to dioxide according to the equation:

$$2Na + WO_3 = Na_2O + WO_2. \quad (4)$$

Sodium oxide reacts further with excess of trioxide:

$$Na_2O + WO_3 = Na_2WO_4. \quad (5)$$

The over-all reaction of the first step of the process will proceed according to the equation:

$$2Na + 2WO_3 = Na_2WO_4 + WO_2. \quad (6)$$

In suitable conditions the formed tungsten dioxide is further reduced to tungsten. We might assume that the further reduction proceeds according to the equation:

$$4Na + WO_2 = 2Na_2O + W. \quad (7)$$

But this is a reaction of the fifth order, and its probability is likewise very low. Evidently the reduction of the dioxide to tungsten proceeds by another route.

Friderich and Sittig [9], when investigating the properties of lower oxides of some metals, established that calcination in vacuum of tungsten dioxide at 1500-1600° leads to decomposition into metallic tungsten and tungsten trioxide; the latter sublimed and was deposited on the cold part of the apparatus. On the other hand, when a pelleted mixture of the trioxide and metallic tungsten was calcined at 1000° in the absence of air, tungsten dioxide was obtained. The authors did not draw any conclusions whatever from these experiments. We may infer that a reversible reaction took place:

$$3WO_2 \rightleftarrows 2WO_3 + W. \qquad (8)$$

It is interesting to note that the thermal effect of this reaction, calculated from thermochemical data [10] at 18°, is 0.1 kcal, i.e. substantially equal to zero.

In normal conditions the equilibrium of reaction (8) is evidently shifted far to the left. If, however, the trioxide could be removed from the sphere of reaction, then the equilibrium would be shifted to the right and reaction (8) would proceed to completion with formation of tungsten. In the experiments of Friderich and Sittig, this was accomplished by using high temperatures (1500-1600°) at which the trioxide sublimed and left the sphere of reaction.

A similar case of an equilibrium shift occurs in the reaction of tungsten dioxide with hydrogen chloride. V. I. Spitsyn and L. I. Kashtanov [11] found that at 400° the following reaction takes place when a stream of dry HCl is passed over tungsten dioxide:

$$3WO_2 + 4HCl = 2WO_2Cl_2 + 2H_2O + W. \qquad (9)$$

Assuming that reaction (8) is valid and allowing for the volatility of tungsten oxychloride, we may propose the following scheme for reaction (9):

$$\begin{aligned} 3WO_2 &\longrightarrow 2WO_3 + W, \\ 2WO_3 + 4HCl &\longrightarrow 2WO_2Cl_2 + 2H_2O. \end{aligned} \qquad (9')$$

For the purpose of experimental verification of the possibility of displacement of the equilibrium of reaction (8), tungsten dioxide was heated in admixture with substances capable of combining with the trioxide formed in reaction (8), thereby shifting the equilibrium to the right. The substances selected had basic properties and were consequently able to combine with tungsten trioxide: sodium pyrophosphate, borax and calcium oxide. The tungsten dioxide required for the experiments was prepared by the method of van-Liempt [12] and G. A. Meerson [13].

Tungsten trioxide in a porcelain boat was reduced in a tube furnace at 850° for 3 hours with purified hydrogen which had been previously saturated with water vapor by passing it through two wash bottles containing water at 85-87°.

Reduction gave a brown powder of tungsten dioxide; the value of x in WO_x was calculated from the analytical data. We selected only those specimens of dioxide in which the value of x was not less than 2, since otherwise the dioxide would have been slightly over-reduced. A small under-reduction was of no consequence.

Sodium pyrophosphate, borax and calcium oxide were prepared in the pure form by the methods described in the literature.

Tungsten dioxide and one of the above-mentioned substances were mixed in a definite ratio and charged into a porcelain crucible; the crucible was placed in an iron bomb which was screwed tight with a cover through an opening in which was led a porcelain tube for passage of a stream of dry, oxygen-free nitrogen.

The bomb, with crucible in position, was first carefully purged with nitrogen and then inserted in a furnace at red heat and kept there for an hour in a current of nitrogen. It was then cooled in a nitrogen stream. After an experiment the melt was lixiviated with water and the reaction products were collected and analyzed. Experimental results are set forth in Table 1.

All the three compounds gave pure metallic tungsten when heated with tungsten dioxide. The yield of tungsten was calculated from reaction (8).

Since none of the substances used is a reducing agent, the formation of metal can only be explained by reaction (8).

TABLE 1

Expt. No.	Added substance	Amount of added substance (in g)	Amount of WO_3 (g)	Molar ratio of added substance to WO_2	Analyzed comp. of WO_2	Reaction temp.	Comp. of obtained product	Yield of tungsten in % of theoretical	Yield of tungsten purity of W by analysis (in %)
1	Sodium pyrophosphate	22.0	3.45	5.17:1	$WO_{2.00}$	1000	Metallic tungsten	72.5	99.2
2	Borax	32.7	2.42	14.5:1	$WO_{2.00}$	920	Ditto	30.6	99.3
3	Calcium oxide . .	2.29	4.41	0.5:1	$WO_{2.08}$	930	"	35.0	99.9

The over-all reaction between the dioxide and the stated compounds may be represented by the following equations:

$$3WO_2 + 2Na_4P_2O_7 = 2Na_2WO_4 + 4NaPO_3 + W, \quad (10)$$
$$3WO_2 + 4Na_2B_4O_7 = 2Na_2WO_4 + 2(Na_2O \cdot 4B_2O_3) + W, \quad (11)$$
$$3WO_2 + 2CaO = 2CaWO_4 + W. \quad (12)$$

At the basis of reactions (10), (11) and (12) are the reactions:

$$Na_4P_2O_7 + WO_3 = Na_2WO_4 + 2NaPO_3,$$
$$2Na_2B_4O_7 + WO_3 = Na_2WO_4 + Na_2O \cdot 4B_2O_3,$$
$$CaO + WO_3 = CaWO_4,$$

of which the over-all expression is (8).

The results of the experiments are sufficiently convincing evidence of the occurrence of reaction (8).

Consequently the reduction of acid tungstates by metallic sodium may be considered to proceed in the following manner. The first stage in reduction of the acid tungstate is reduction of tungsten trioxide with formation of dioxide according to equations (4) and (5). The further course of the process depends on the state of equilibrium of reaction (8). The state of this equilibrium in the given conditions is determined by the properties of the medium. If the medium is basic, then the tungsten trioxide is bound and the equilibrium of (8) is shifted to the right in the direction of formation of metal. In an acid medium the equilibrium is shifted to the left and metal is not isolated.

When acid sodium tungstates are reduced, there will correspond to the basic or acidic character of the medium, respectively, an excess or deficiency of the sodium necessary for reduction of the whole of the free (excess) tungsten trioxide to metal. Let us consider this case more closely.

1. Excess of sodium. The reduction reaction proceeds in the following manner:

$$3WO_3 + 6Na = 3WO_2 + 3Na_2O,$$
$$3WO_2 = 2WO_3 + W,$$
$$2WO_3 + 2Na_2O = 2Na_2WO_4.$$

The residue of sodium oxide is bound by free trioxide:

$$Na_2O + WO_3 = Na_2WO_4.$$

The sum of these reactions gives equation (3).

The reaction leads to separation of metallic tungsten.

2. Deficiency of sodium. There is an excess of tungsten trioxide in the medium. At the start, as in the preceding case, tungsten dioxide is formed, while sodium oxide is bound by excess of tungsten trioxide.

But due to the excess of trioxide, equation (8) will be shifted to the left. Hence the tungsten dioxide will not be decomposed with formation of tungsten, but dioxide will accumulate.

Tungsten dioxide is bound to form a bronze with sodium tungstate in accordance with Brunner's reaction:

$$Na_2WO_4 + WO_2 = Na_2W_2O_6 \quad (13)$$

and then, in presence of excess trioxide:

$$Na_2W_2O_6 + WO_3 = Na_2W_3O_9 \quad (14)$$
$$Na_2W_3O_9 + WO_3 = Na_2W_4O_{12}. \quad (15)$$

Consequently, when acid tungstates are reduced with a deficiency of sodium, bronzes are certain to be formed and they are consequently products of incomplete reduction of acid tungstates.

V. I. Spitsyn showed that when acid tungstates are reduced with hydrogen the degree of reduction of the obtained bronzes increases with increasing amount of reducing agent. The bronzes may be arranged in the following order of increasing degree of reduction: blue, violet, red, golden yellow. Similarly in reduction with sodium the degree of reduction must increase with increasing amount of sodium.

In our preceding paper we introduced the concept of the critical value of the sodium amount. By this term is to be understood the ratio (in %) of(on the one hand)the amount of sodium necessary for reduction of all the free trioxide to tungsten and neutral tungstate to (on the other) the amount of sodium necessary for complete reduction both of the trioxide and of all the neutral tungstate according to the equation:

$$Na_2WO_4 + 6Na = 4Na_2O + W$$
$$\text{and } WO_3 + 6Na = 3Na_2O + W.$$

If the amount of sodium used for reduction is less than the critical value, then an excess of trioxide remains and bronzes must be formed. Consequently the critical value may be regarded as a limiting value below which bronzes are obtained and above which tungsten is obtained.

The literature does not contain any data about the preparation of bronzes with the help of metallic sodium. It was therefore of interest to undertake a series of experiments on the reduction of acid tungstates by sodium. Reduction was accomplished in an iron bomb at 800-900°. After an experiment, the reaction mass was lixiviated with water and the character of the products was determined. The experimental results are set forth in Table 2. The amount of sodium (in %) was calculated in relation to the theoretical amount of sodium necessary for complete reduction of all the tungstate. In the sixth column are the critical values of sodium calculated for tungstate of the given composition.

The experimental results show that reduction of acid tungstates with an inadequate amount of sodium leads to tungsten dioxide and bronzes. The limiting character of the critical value of sodium is here very clearly illustrated. In all cases, when the amount of sodium even very slightly exceeds the critical value, metal is formed. If the amount of sodium is below this critical value, we obtain bronzes, tungsten dioxide or a mixture of these with metal.

When there is little tungsten trioxide in the starting mixture, reduction gives mainly dioxide. When there is a large proportion of trioxide we obtain bronzes. The closer the amount of sodium approaches to the critical value, the higher the degree of reduction and, conversely, with decreasing amount of sodium the degree of reduction correspondingly decreases. In this case we observe the same sequence as was established by V. I. Spitsyn for reduction of acid tungstates with hydrogen.

Such a sequence in the reduction of acid tungstates is fully explained by the above scheme. With an excess of trioxide the equilibrium of equation (8) is shifted in the direction of formation of dioxide which, as already shown, combines with tungstates to form bronzes in accordance with equations (13) to (15).

There is every reason for assuming that these reactions are reversible. Brunner showed that bronzes are capable of decomposing according to a reversible reaction, for example:

$$3Na_2W_2O_6 \rightleftarrows 3Na_2WO_4 + 2WO_3 + W.$$

But the last two terms of this equation are in equilibrium with WO_2 according to reaction (8).

On calculating the second equation from the first, we arrive at equation (13a) in analogy with equation (13):

$$3Na_2W_2O_6 \rightleftarrows 3Na_2WO_4 + 3WO_2. \quad (13a)$$

On the other hand, as already indicated above, we know from Philipp's work that bronzes are capable of enrichment or impoverishment in tungsten trioxide by fusing them with salts containing an excess or deficiency of trioxide. Consequently equations of the type of (14), (15), etc. are likewise reversible.

TABLE 2

Expt. No.	Composition	Amount (in g)	Amount of Na (% of theory)	Crit. val. of Na (%)	Reaction products
1	Eutectic: Na_2WO_4 80 mole-%, WO_3 20 mole %	22.2	2.02	5.0	Tungsten dioxide
2	Ditto	25.0	2.08	5.0	Tungsten dioxide
3	"	24.0	4.0	5.0	Mixture of tungsten dioxide and tungsten
4	"	14.5	5.2	5.0	Tungsten
5	"	25.0	6.3	5.0	Tungsten
6	Ditungstate $Na_2W_2O_7$	20.0	2.95	12.5	Mixture of tungsten dioxide and tungsten bronze
7	Ditto	20.0	6.2	12.5	Tungsten dioxide
8	"	15.0	12.7	12.5	Tungsten
9	Paratungstate $5Na_2O \cdot 12WO_3$	20.0	1.96	14.58	Mixture of red and violet bronzes
10	Ditto	20.0	4.2	14.58	Blue bronze (640°)
11	"	20.0	12.0	14.58	Golden-yellow bronze
12	"	25.0	17.6	14.58	Tungsten
13	"	20.0	26.5	14.58	Tungsten

On this basis we may conclude that reactions (8), (13), (14), (15), etc. form a group of closely linked reactions.

Decrease of Na ↓

$$2WO_3 + W \rightleftarrows 3WO_2 \quad (8)$$

$$Na_2WO_4 + WO_2 \rightleftarrows Na_2W_2O_6 \quad (13)$$

$$Na_2W_2O_6 + WO_3 \rightleftarrows Na_2W_3O_9 \quad (14)$$

$$Na_2W_3O_9 + WO_3 \rightleftarrows Na_2W_4O_{12} \quad (15)$$

↑ Increase of Na

With decreasing amount of sodium taken for the reduction, the amount of residual trioxide increases and the equilibrium of all the above reactions will be shifted to the right and downward, i.e. in the direction of formation of less reduced bronzes. With progressive increase of the sodium amount, the amount of residual trioxide will decline and the equilibrium of the whole group of reactions will be shifted to the left and upward. Hence we begin to get an increasing amount of dioxide — the last stage of reduction on the route to tungsten. As soon as the amount of sodium exceeds the critical amount, the latter stage of reduction will be attained and formation of tungsten will commence.

Consequently with gradual increase in the content of sodium and correspondingly gradual decrease in the quantity of trioxide, the reaction products pass successively through all the stages of reduction on the way to metal. The whole group of these reactions constitutes a unified complex in which each individual reaction is closely linked with all the others. This also accounts for the fact that usually we always obtain a mixture of bronzes, the separation of which into pure constituents is a rather complex problem when sufficient excess of trioxide is present.

SUMMARY

1. A study was made of the mechanism of reduction of acid sodium tungstates by metallic sodium. It was shown that this reaction proceeds in two stages. Tungsten dioxide is formed in the first stage. The second stage depends on the character of the medium and is governed by the state of equilibrium of the reversible reaction:

$$3WO_2 \rightleftarrows 2WO_3 + W.$$

2. It was established that when acid tungstates are reduced by sodium, the character of the reaction products depends on the degree of acidity of the medium. If the amount of sodium taken for the reduction is sufficient to impart a basic character to the medium, then the equilibrium of equation (8) will be shifted to the right, in the direction of formation of metallic tungsten. When there is a deficiency of sodium and the medium has an acidic reaction, then equation (8) is shifted to the left, in the direction of formation of tungsten dioxide.

3. The possibility was demonstrated of obtaining tungsten bronzes by the action of metallic sodium on acid sodium tungstates. The conditions of formation and the mechanism of formation of bronzes were clarified. It was established that the character of the resulstant bronzes depends on the acidity of the medium and is governed by the state of equilibrium of a group of reversible reactions which are closely linked with one another.

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